Synthesis by sol-gel route and characterization of Yttria Stabilized Zirconia coatings for thermal barrier applications

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Abstract

This paper deals with the development of new synthesis techniques for functional materials such as Yttria Stabilized Zirconia (YSZ) used in the field of thermal barriers coatings. Currently, Thermal Barrier Coatings (TBCs) are manufactured by dry route technologies (EB-PVD or plasma spray) but such methods are directional and often require costly investments and complicated operations. We have carried out significant work aimed at developing sol-gel routes, which are nondirectional methods, to prepare, by suitable chemical modifications, nanocrystalline materials with a controlled morphology. The main advantage of this method is to decrease the crystallization temperature, much lower than the conventional processes, allowing the synthesis of reactive powders with nanometric particles size. In this paper, the formulation of an alkoxide sol has been optimized in order to obtain homogeneous YSZ films. Nature and quantity of binders have been studied. Superalloys have been then immersed in the sol and withdrawn at several controlled rates before being annealed at different temperatures. The films microstructures have been investigated using scanning electron microscopy. It appears that the combination of a slower withdrawal speed (17 cm/min) with a 3 wt.% content of DBP allows to obtain the most homogeneous and the thicker coatings. Moreover, SEM-FEG observations have shown that the deposit is present all over the rough surface of the substrate and is composed of two morphologies: a YSZ thin covering film and a thicker discontinuous layer duplicating the substrate topography.

Keywords: Sol-gel; Yttria Stabilized Zirconia

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1. Introduction

Thermal Barrier Coatings (TBCs) are used as insulators on hot section components to reduce operating temperatures in aircraft engines, marine propulsion and industrial gas turbine. The TBC system corresponds to two layers: the ceramic top coat (about 250 µm) and the bond coat (about 150 µm). The top coat mainly consists of Yttria Stabilized Zirconia (YSZ) with a low thermal conductivity. The bond coat is based on aluminoformer compounds generally MCrAlY, M = Ni and/or Cr or Co [1], [2], [3] and [4] or Pd or Pt modified aluminides [5], [6] and [7]. At an industrial scale, two dry-route processes are used: the plasma spraying (PS) and the Electron Beam Physical Vapour Deposition (EBPVD). By these processes, coatings have different microstructures: lamellar microstructure consisting in splats superposition for PS coatings with thermal conductivity in the range from 0.7 to 0.9 W m^{-1} K^{-1} [8] and column-like microstructure for EBPVD coatings with best mechanical performances. However, in this last case, perpendicular orientation of the columns makes that thermal conductivity is twice higher compared to PS coating.

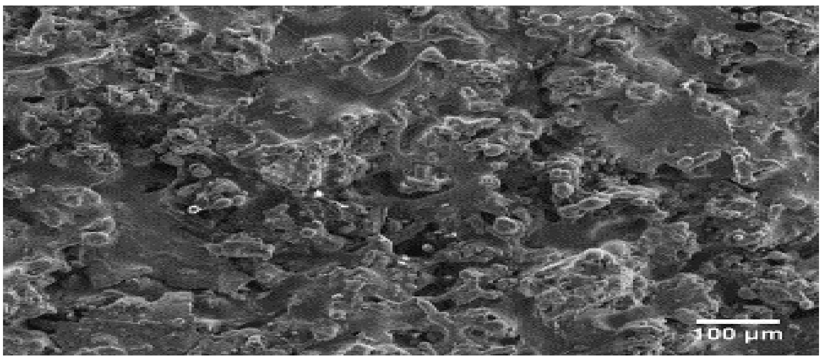
Nowadays, works to lower the ceramic thermal conductivity, keeping good mechanical properties, have been carried out on the nature of the elements being able to replace zirconia in TBC systems [9], [10] and [11]. However, in this case, the modification of the microstructure coating is a key point. The orientation and the number of pores in the coating are important parameters [12], [13] and [14]. This study precisely tackles this problem and a new process for thermal barrier applications is proposed consisting in a chemical route which is the sol-gel process. It is a versatile process able to produce either thin ceramic coatings or thick deposits [15] and [16]. The main advantage of this method is to decrease the crystallization temperature, much lower than the conventional processes. This allows to synthesize reactive nanometric powders. Moreover, the sol-gel process is a non-directional deposition technique, which is very different to the PS or the EBPVD methods. Consequently, multilayers with graded porosity can be prepared. The key point in this last case is the formulation of stable slurries. More precisely, the choice of solvent, binder and other additives, are important factors.

This paper presents the first films obtained by dip-coating the substrate in a standard YSZ sol. Sol parameters and dip-coating conditions have been optimized in order to obtain thicker and homogeneous layers on rough NiCrAlY substrates.

2. Experimental

The substrate consists of Ni-based superalloys (Hastelloy X), covered by a NiCrAlY bondcoat, plasma sprayed under air. The surface topography is represented on Fig. 1 using Secondary Electron Microscopy (SEM). Its roughness, essential to allow the adherence of the YSZ plasma sprayed top coat, is very high in the range [10; 15 μm]. Such an important roughness is completely unusual with regard to the sol-gel process and the deposition of thick and covering layers (∼ 250 μm) on such substrates is a real challenge because the substrate wettability towards sols is not constant in this case.

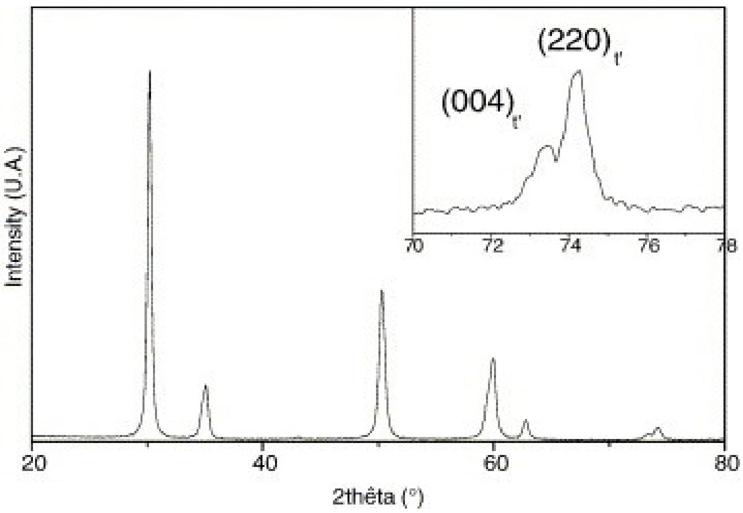
Fig. 1. Surface of NiCrAlY bond coat obtained by plasma spray, under air.



The starting precursors are the zirconium (IV) propoxide ($Zr(OPr)_4$) (Aldrich), yttrium (III) nitrates hexahydrate (Acros Organics) and the solvent is 1-propanol. A complexing agent, acetylacetone (AcAc), has been used to reduce the zirconium alkoxide reactivity towards water and to avoid hydroxides formation. The two molar ratio $AcAc/Zr(OPr)_4$ and $H_2O/Zr(OPr)_4$ reported in a previous paper [18] have been kept constant respectively to 0.8 and 9.5.

A crystallographic study has already shown that YSZ powders obtained after calcination at 950 °C (heating rate: 100 °C/H) are crystallized in the tetragonal symmetry (space group: $P4_2/nmc$) [17] and [18]. Fig. 2 shows a X-ray diffraction pattern of YSZ powder with a 10 mol% $YO_{1,5}$ content.

Fig. 2. X-rays pattern of the YSZ powder produced using the sol-gel route after heat treatment.



Layers are prepared by immersion of the substrates in the sols and withdrawn at a controlled speed. Then, samples are dried at room temperature and then heat treated. Two heat treatments have been performed: A) 2 h step at 950 °C (heating rate: 100 °C/H) and B) 30 min at 1150 °C followed by a 4 h step at 950 °C (heating rate: 100 °C/H). The higher temperature of the heat treatment B (1150 °C) corresponds to the maximum applicable temperature for the superalloy. Furthermore, the maximal dwell time must not exceed 30 min. An effect on the coating morphology is expected to be observed by increasing the sintering temperature of the YSZ nanoparticles.

Microscopic characterizations have been performed using a SEM *Jeol JSM6400* and a SEM with Field Emission Gun (SEM-FEG) *Jeol-6700F*.

3. Results and discussion

3.1. Sol pre-deposit

Considering the important anfractuosities of the substrate, a preliminary YSZ sol deposit playing the role of chemical interface between NiCrAlY bond coat and next thicker layers is necessary to increase adhesion.

Several parameters have been studied to obtain homogeneous deposits. In particular, the influence of the nature and the amount of binders was studied in order to improve the behavior of the sol during the dip-coating. So, two binders were used: the dibutylphtalate (DBP) and an equimassic mixture of DBP and polyethyleneglycol (PEG). Moreover, two viscosities of sol were studied (5 and 100 mPa s). Finally, two withdrawal speeds and two heat treatments were performed.

3.1.1. Series I-a, influence of the binders and the heat treatments

Several samples were prepared from a sol with a low viscosity (5 mPa s), by varying the nature and the amount of binders. The heat treatments A and B were performed for each composition. The withdrawal speed was kept equal to 25 cm/min in these series. The Table 1 (samples I-1 to I-15) gathers the data.

Table 1.

Pre-deposit of sol, data concerning the series I-a and I-b of samples

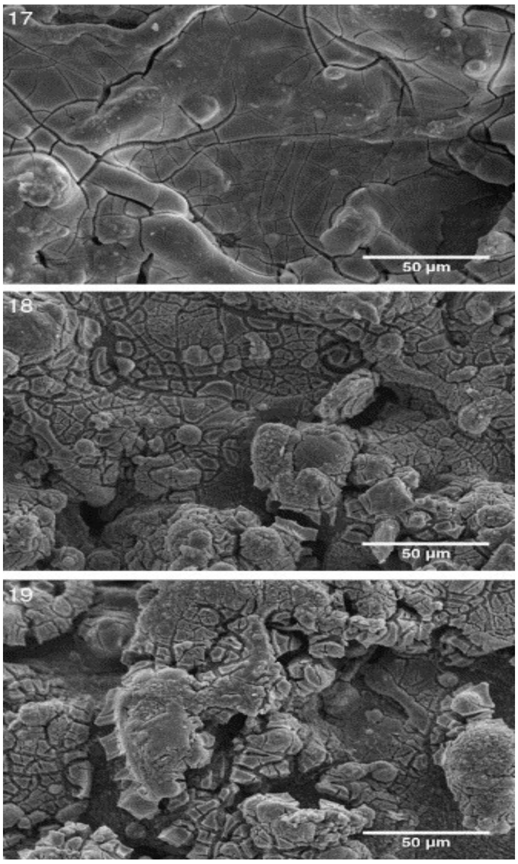
Samples	Withdrawal speed (cm min^{-1})	DBP (wt.%)	PEG/DBP (wt.%)	Heat treatment
SERIES I-a, viscosity of the sol: 5 mPa s				
I1	25	0	–	–
I2	25	0	–	A
I3	25	0	–	B
I4	25	0.5	–	–
I5	25	0.5	–	A
I6	25	0.5	–	B
I7	25	1.5	–	–
I8	25	1.5	–	A
I9	25	1.5	–	B
I10	25	–	0.5	–
I11	25	–	0.5	A
I12	25	–	0.5	B
I13	25	–	1.5	–
I14	25	–	1.5	A

Samples	Withdrawal speed (cm min^{-1})	DBP (wt.%)	PEG/DBP (wt.%)	Heat treatment
I15	25	–	1.5	B
SERIES I-b viscosity of the sol: 100 mPa s				
I16	17	–	–	–
I17	17	–	–	A
I18	17	–	–	B
I19	17	–	1.5	–
I20	17	–	1.5	A
I21	17	–	1.5	B
I22	25	–	3.0	–
I23	25	–	3.0	A
I24	25	–	3.0	B
I25	17	–	3.0	–
I26	17	–	3.0	A
I27	17	–	3.0	B
I28	25	–	5.0	–
I29	25	–	5.0	A
I30	25	–	5.0	B
I31	17	–	5.0	–
I32	17	–	5.0	A
I33	17	–	5.0	B

From a macroscopic point of view, each heat treated sample is covered of a thin white film, corresponding to YSZ material.

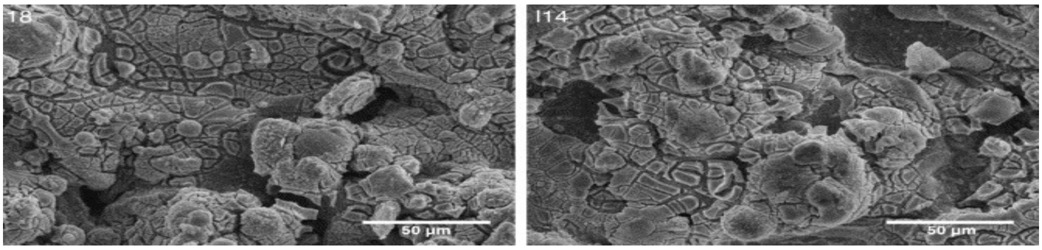
SEM characterizations of the series have shown that each deposit is cracked before and after heat treatment. Heterogeneities (length and thickness) are more important after the heat treatments A and B (Fig. 3).

Fig. 3. Series I-a, influence of the heat treatment with a constant amount of binder (case of DBP) : I-7 = no heat treatment, I-8 = cycle A, I-9 = cycle B.



No difference was underlined between the two binders. For example, Fig. 4 presents samples prepared with a content of 1.5 wt.% DBP or DBP/PEG mixture and heat treated by the protocol A. Samples surfaces are similar. This cracking phenomenon is partly due to the quick densification of the YSZ material during the thermal treatment. This calcination leads to the widening of the cracks after the removal of organic compounds but the main point is the important anfractuosities of the NiCrAlY substrate. In order to obtain thicker deposits and for a better accommodation of thermomechanical stresses by the film, the increase of the binder content and of the sol viscosity should be favourable. The withdrawal speed is also an important physical parameter to control.

Fig. 4. Series I-a, effect of the nature of the binder compared with the heat treatment. I-8 (1.5 wt.% DBP) and I-14 (1.5 wt.% DBP/PEG) after the heat treatment A.



3.1.2. Series I-b, influence of the amount of DBP and of the withdrawal speed

In this series (Table 1, samples I-16 to I-33), only DBP was used as binder. The DBP content, up to 5 wt.%, was higher compared to the series I-a. Two withdrawal speeds have been studied. In these experiments, the sol viscosity was equal to 100 mPa s.

From macroscopic observations, no difference was put in evidence concerning the adherence of the deposit and the samples are easy to handle. They are recovered of a whiter, consequently thicker, deposit than the series I-a (estimated between 5 and 10 µm). In fact, the samples obtained with a DBP content of 3 wt.% and with a lower withdrawal speed (17 cm/min) are optimal. Indeed the samples I26 and I27 are the most homogeneous and the whitest. No difference between both heat treatments (A and B) have been underlined.

SEM characterizations of the surfaces show that the deposit is cracked at a macroscopic scale (Fig. 5). But, as presented on Fig. 6, a SEM-FEG observation inside the cracks of I-27 put in evidence that the YSZ deposit resulting from the sol-gel process is perfectly covering and is present on the whole surface of the NiCrAlY substrate (see locations 1, 2 or 3 on Fig. 6). We can underline two deposit zones: the first one consists of a superficial film of YSZ aggregates and the second one is a very thin, homogeneous and covering film of YSZ material directly at the interface. Thus, the deposit can be observed in several zones due to the irregular topography of the substrate as shown on the Fig. 6.

Fig. 5. SEM characterization of I-27 (Series I-b), viscosity of the sol: 100 mPa s, 3 wt.% DBP, speed of withdrawal: 17 cm/min, heat treatment A.

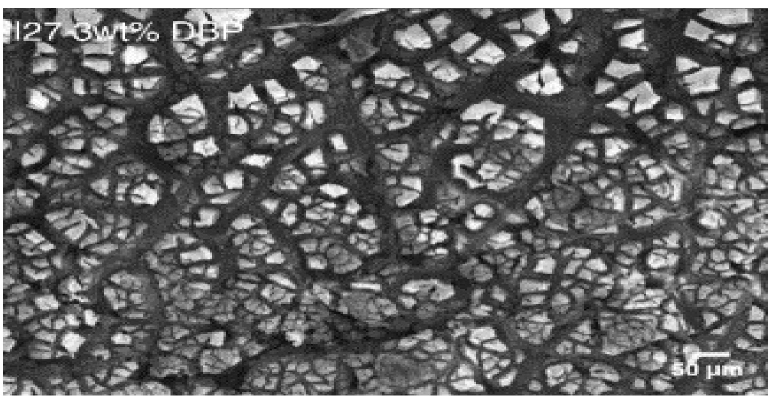
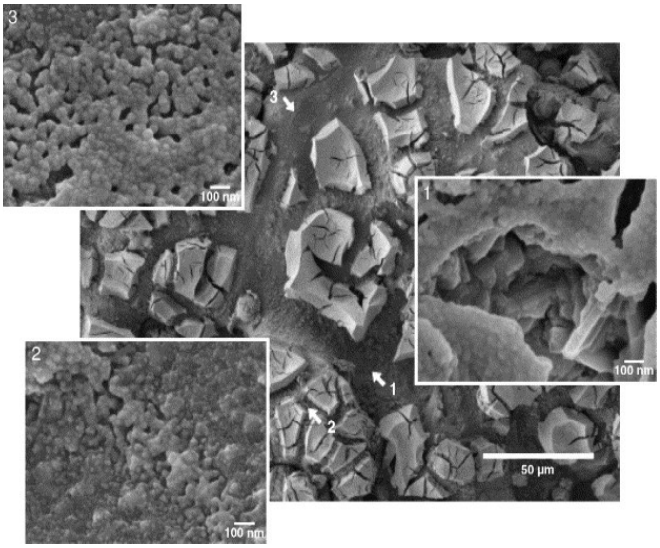


Fig. 6. SEM-FEG characterization of YSZ deposit by the sol-gel process (sample : I-27).



4. Conclusion

By optimizing the sol formulation, it has been possible to obtain homogeneous YSZ coatings by sol-gel route. This study was the first step to create an adequate chemical interface between NiCrAlY bond coat and next thicker layers. Now, the next step is to deposit thicker layers thanks to composite sols because target thickness, for thermal barrier applications, is around 200 µm. Composite sols are constituted by YSZ sol-gel powders directly incorporated in the YSZ precursor sol. Optimization of these composite sols (powders granulometry and content) is now in progress.

Acknowledgments

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